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14. ABSTRACT Polyhedral oligomeric silsesquioxane (POSS) has generated much interest in the development of novel nanomaterials. The organic groups attached to the silicon atoms in the POSS cage can serve many different functions. It has been shown that POSS copolymers exhibit different rheological properties when the organic group is changed in a copolymer. In this work, we examine the effects of varying the organic groups (R = c-C ₅ H ₉ ; denoted as Cp, <i>i</i> -C ₄ H ₉ ; ⁱ Bu, C ₃ H ₄ F ₃ ; FPr) on propylmethacryl POSS molecule copolymerized with n-butyl methacrylate. ⁱ Bu groups increase the free volume in the copolymer whereas the Cp and FPr groups appear to interact thereby reinforcing the soft polymer.					
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Abstract

Polyhedral oligomeric silsesquioxane (POSS) has generated much interest in the development of novel nanomaterials. The organic groups attached to the silicon atoms in the POSS cage can serve many different functions. It has been shown that POSS copolymers exhibit different rheological properties when the organic group is changed in a copolymer. In this work, we examine the effects of varying the organic groups ($R = \text{c-C}_5\text{H}_9$: denoted as Cp, $i\text{-C}_4\text{H}_9$: $i\text{Bu}$, $\text{C}_3\text{H}_4\text{F}_3$: FPr) on propylmethacryl POSS molecule copolymerized with n-butyl methacrylate. $i\text{Bu}$ groups increase the free volume in the copolymer whereas the Cp and FPr groups appear to interact thereby reinforcing the soft polymer.

Effect of Polyhedral Oligomeric Silsesquioxane (POSS) Substituents on the Rheological Behavior in Butyl Methacrylate/POSS Copolymers

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INTRODUCTION

Polyhedral oligomeric silsesquioxane (POSS) has generated much interest in the development of novel nanomaterials. POSS has an inorganic silicon oxide core with each silicon bonded to one organic moiety yielding the empirical formula $(\text{RSiO}_{1.5})_n$, $n = 8, 10$ or 12 . The discrete particle size is on the order of ~ 1.5 nm.¹ The organic groups attached to the silicon atoms in the POSS cage can serve many different functions. If the organic groups are identical and nonfunctional then the POSS can be blended into an existing polymer to yield increase toughness, crystallization rate or hydrophobicity.²⁻⁴ The organic groups can be identical and functionalized where POSS molecules can be used as cross-linking agents and yield membranes or fire retardant materials.⁵⁻⁶ Another POSS molecule has one or two of the organic groups functionalized forming a copolymer. These systems can lead to improved properties such as increased glass transition temperature, solvent or atomic oxygen resistance.⁷⁻¹¹

In this work, we examine the effects of varying the organic groups ($R = \text{c-C}_5\text{H}_9$: denoted as Cp, $i\text{-C}_4\text{H}_9$: 'Bu, $\text{C}_3\text{H}_4\text{F}_3$: FPr) on propylmethacryl POSS molecule copolymerized with *n*-butyl methacrylate.

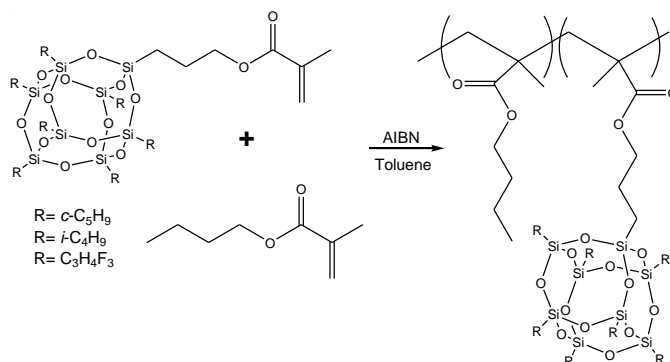
EXPERIMENTAL

Materials. Toluene (Fisher) and CDCl_3 (Cambridge Isotope Laboratories, Inc) were dried and the inhibitor was removed from *n*-butylmethacrylate (Aldrich) prior to use.

Synthesis. POSSpropylmethacryl-*co*-*n*-butylmethacrylate polymers containing 0, 3, 5, 10 or 20 wt % POSSpropylmethacrylate monomer were synthesized (Scheme 1): each set with a different POSS substituent. To maintain similar degrees of polymerization, a 25 molal monomer solution containing a total of 3 grams of monomers was initiated using 0.25 mole % azobis(isobutyronitril) (AIBN). An example synthesis for 10 wt. % POSS follows: under a nitrogen atmosphere, a dry oxygen free solution of toluene (2.70 mL), [(propylmethacryl)(*i*-C₄H₉)₇(Si₈O₁₂)] (300 mg, 0.317 mmol), *n*-butylmethacrylate, (2700 mg, 18.99 mmol) and AIBN (7.75 mg, 0.0481 mmol) was heated to 65 °C for 24 hours. Polymer was purified by diluting with 15 mL of CHCl_3 and precipitated into 80 mL of methanol. The mixture was stirred for 24 hours. Purification was repeated twice, dissolving the product in chloroform and diethyl ether, respectively. The polymer was dried at 60 °C under vacuum overnight. Greater than 90% of the theoretical yield was obtained for each polymer.

Characterization. ¹H NMR data was obtained on a Bruker 300 MHz or 400 MHz instrument as CDCl_3 solutions. The chemical shifts were reported in parts per million (δ ppm). The spectra obtained with an eight second delay between pulses and referenced to the CDCl_3 shift at δ 7.26 ppm. Molecular weights were determined using gel permeation chromatography (GPC) and a combination of refractive index and multi-angle laser-light scattering measurements on a Wyatt Technology Corporation HELIOS spectrometer. Differential scanning calorimetry (DSC) experiments were performed on a TA Instruments Q100, glass transition temperature, T_g , was reported from the second heating scan at 10 °C/min from the half height of the enthalpic step. Rheological measurements were obtained on an Anton Paar MCR 500

rheometer in parallel plate configuration (gap width = 1.5 mm). Storage modulus (G'), loss modulus (G'') and damping factor ($\tan \delta$) were measured as a function of frequency at 150 °C.



Scheme 1. Copolymerization of propylmethacryl POSS with *n*-butylmethacrylate.

DISCUSSION

All polymers were successfully synthesized, demonstrated via ¹H NMR with M_w in excess of 3000 g/mol denoting entanglement¹² (results not shown). The T_g of the butyl methacrylate-*co*-POSS polymers is shown in Table 1. The T_g of Cp and FPr show a marked increase with increasing POSS content while the T_g of the 'Bu remains the same.

Table 1. T_g for Butyl Methacrylate-*co*-Propyl Methacryl POSS Polymers with Various POSS Substituents

	T_g (°C)		
	Cp	'Bu	FPr
0%	35.8	37.0	35.5
3%	37.2	37.1	
5%	38.0	37.7	
10%	38.7	37.1	36.7
20%	41.4	37.2	39.4

Figure 1 presents G' dependence on the angular frequency with a) cyclopentyl POSS, b) iBu POSS, and c) trifluoropropyl POSS. Interestingly the FPr POSS copolymers (Fig. 1c) show an increase in G' with increasing POSS % at all frequencies. This observation along with the increase in the T_g suggests that the FPr POSS may be aggregating thereby forming an anchoring phase that suppresses the relaxation of adjacent soft segments. Conversely, the 'Bu (Fig 1b) POSS exhibits a lower G' than the 0% with increasing POSS content. This suggests that copolymerization with 'Bu POSS increases free volume through a plasticization effect although there is a lack of T_g change. This is consistent with Wu et al¹³, who reported a decrease in T_g with increasing 'Bu POSS content attributed to the "branching" nature of the POSS copolymers consequently increasing free volume. Finally, the Cp POSS copolymers exhibit higher values of G' at low frequency in comparison with the control: suggesting the existence of POSS-POSS interactions. Interestingly, in the 20 wt.% containing copolymer, interactions between side groups appear to be compromised by high frequency shear. The Cp POSS copolymers exhibit more solid-like behavior at low frequencies in comparison with the control while the opposite is true for 'Bu POSS.

Conclusions

It has been shown that POSS copolymers exhibit different rheological properties when the organic group is changed in a copolymer. iBu POSS appears to increase the free volume in the copolymer whereas the Cp groups in general appear to interact through aggregation when probed at low shear rates, however, at high

concentrations, such interactions are severed during high frequency shear and the side groups contribute to an increase in free volume. Alternatively, copolymerization with FPr POSS increases G' with increasing POSS wt.% at all frequencies, potentially resulting from stronger POSS-POSS interactions.

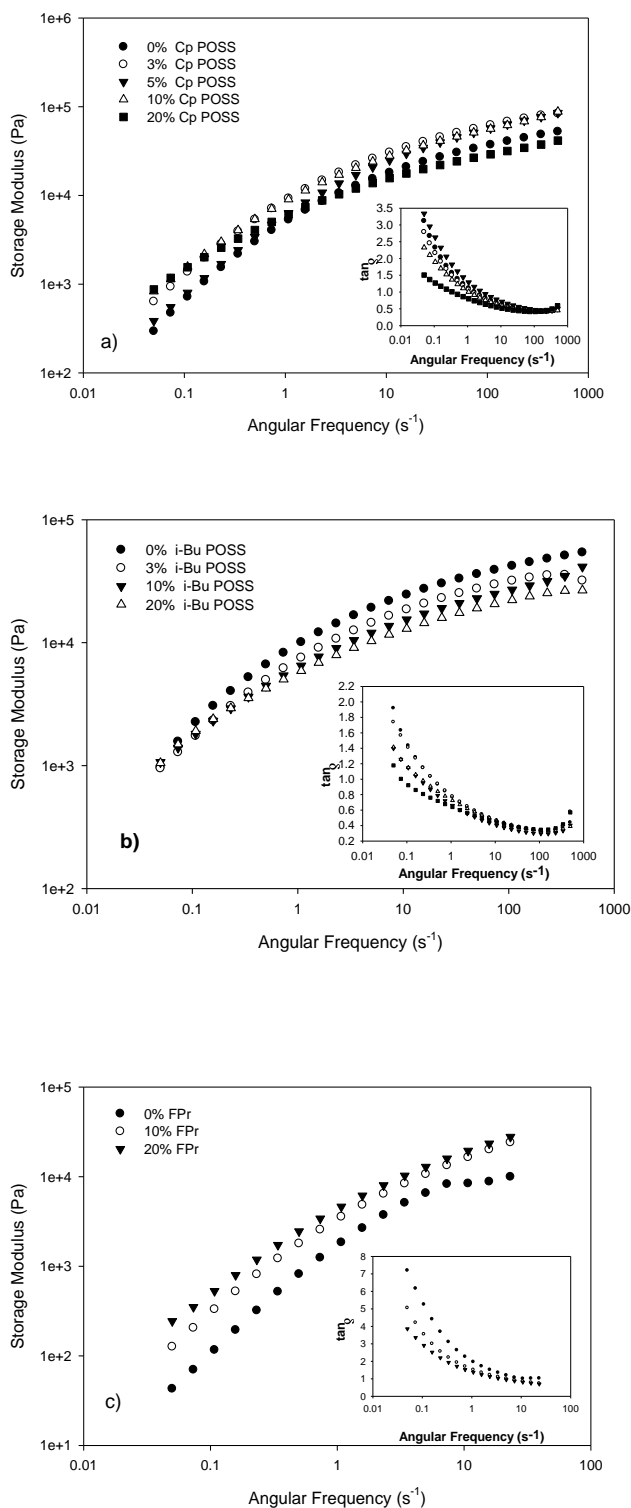


Figure 1. Dependence of the storage modulus on the angular frequency of poly butyl methacrylate-co- R-POSS Inset: Dependence of angular frequency on the $\tan\delta$ a) R=cyclopentyl b) R=iso-butyl c) R=trifluoropropyl

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